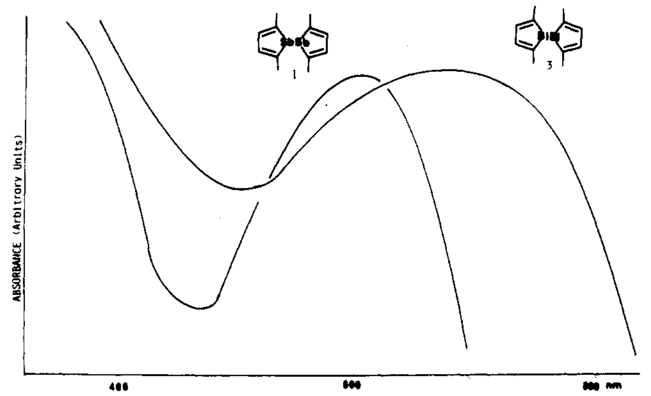
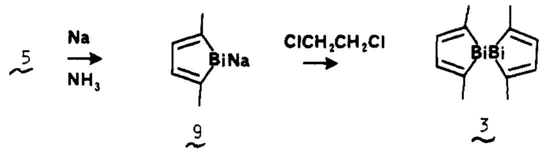


Figure 1. A comparison of the diffuse reflectance spectra of solid 2,2′,5,5′-tetramethylbistibole (1) and 2,2′,5,5′-tetramethylbibismole (3). The vertical scale is arbitrary.

(s, 6 H), 7.28–7.45 (m, 3 H), 7.98 (d, J = 6.5 Hz, 2 H), 8.53 (s, 2 H); MS m/e (relative intensity) 366 (1, M^+ for $C_{12}H_{13}Bi$), 209 (60, Bi^+), 157 (100, $M^+ - Bi$). Because of its lability the bismole was used directly without extensive purification. Like its pnicogen analogues, 1-phenyl-2,5-dimethylbismole undergoes facile phenyl cleavage on treatment with active metals.[7,12] The reaction of **5** with sodium in liquid ammonia gave the potentially aromatic 2,5-dimethylbismolyl anion **9**. Coupling of **9** with 1,2-dichloroethane afforded the desired 2,2′,5,5′-tetramethylbibismole (**3**): mp > 95 °C dec; ^1H NMR (C_7D_8) δ 2.41 (s, 6 H), 8.43 (s, 2 H); ^{13}C NMR (C_7D_8) δ 28.5 (CH_3), 152.3 (CH), 162.6 (CBi); MS (CI–CH_4) m/e (relative intensity) 579 (0.5, $M^+ + 1$ for $C_{12}H_{16}Bi_2$), 209 (16), 160 (100, $M^+ - Bi_2$). Anal. Calcd for $C_{12}H_{10}Bi_2$: C, 24.93; H, 2.79. Found: C, 24.81; H, 2.77.



This dibismuthine is air sensitive but in the solid state can be stored at room temperature. The dibismuthine is obtained as black crystals with a greenish luster. The diffuse reflectance spectrum of crystalline **3** (illustrated in Figure 1) shows a broad absorption maximum centered at 690 nm. On the other hand, solutions of **3** in cyclohexane are red (λ_{max} = 230 nm (ϵ 14 600), sh 320 nm (5600) with a low intensity tail out to 700 nm). This large red shift between solution and solid is similar to that observed for **1**. Consequently, we believe that the crystal packing of **1** and **3** must be similar.

Hoffmann et al. have suggested that the solid-phase color of **1** is due to a $\sigma \rightarrow \pi^*$ excitation.[2] One expects the lowest π^* orbital of **1** and **3** to be of very similar energy. On the other hand, the Bi–Bi σ bond of **3** is likely to be of higher energy than the Sb–Sb σ bond of **1**.[4] Thus the observed red shift between **3** and **1** is consistent with the smaller band gap predicted from the Hoffmann model.

Acknowledgment. Support of our work by the A.F. O.S.R. (Grant No. 81-099) is gratefully acknowledged.

Registry No. **3**, 88635-82-9; **4**, 77214-60-9; **5**, 88635-81-8; **6**, 88635-79-4; **7**, 88635-80-7; **9**, 88644-52-4; $C_6H_5BiI_2$, 39110-03-7.

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Mixed-Metal Cluster Carbides and a Mixed-Metal Ketenylidene with Nucleophilic Carbide Sites

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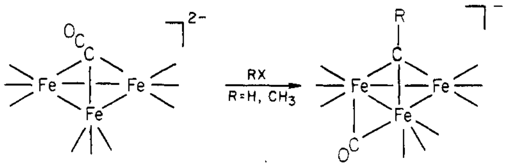
Summary: The nucleophilic ketenylidene $[Fe_3(CO)_9(CCO)]^{2-}$ (III) serves as a convenient mixed-metal carbide precursor. Compound III reacts readily with labile metal carbonyl fragments such as $M(CO)_3(NCCH_3)_3$ (M = Cr, W) to generate the new clusters $[Fe_3MC(CO)_{13}]^{2-}$ which contain a nucleophilic carbide ligand similar to that in $[Fe_4C(CO)_{12}]^{2-}$. By contrast, treatment of III with $Co_2(CO)_8$ leads to replacement of one iron vertex, generating a new monoanionic heterometallic ketenylidene $[Fe_2Co(CO)_9(CCO)]^-$ which is less reactive but otherwise chemically similar to III. X-ray crystallographic analysis shows the CCO tilt to be considerably less than in the $[Fe_3(CO)_9(CCO)]^{2-}$ species.

Because of the importance of CO cleavage on metal surfaces and the subsequent reduction of the surface carbide, there is considerable interest in the chemistry of metal cluster compounds containing reactive carbide ligands. Metal cluster carbides having more than four metal atoms have repeatedly been observed to lack reactivity at the carbide center.[2,3] To date, reactivity of the carbide ligand has been achieved only for the isoelectronic four-iron butterfly carbides, $Fe_4(CO)_{13}C$ (I) and $[Fe_4(CO)_{12}C]^{2-}$ (II).[4,5] In these compounds the carbide ligand is coordinated to only four iron atoms and it is exposed. Recently, a three-iron cluster $[Fe_3(CO)_9(CCO)]^{2-}$ (III) was synthesized which contains a ketenylidene ligand, CCO, having carbide-like reactivity, and this discovery raises the possibility that ketenylidenes may play a role in the reduction of CO on metal surfaces.[6] The reactivity of III is illustrated by its interaction with methylating agents or acids to produce ethylidyne or methylidyne derivatives (eq 1), with concomitant migration of the ketenyl CO onto the metal cluster. In the present communication we report that III affords a convenient route to new mixed-metal cluster



(1)

III

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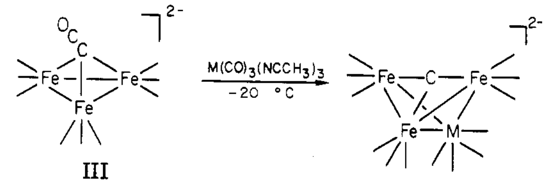
carbides and to a new ketenylidene, all of which have reactivity at the carbide carbon.

In analogy with known metal cluster building reactions,[7,8] $[Fe_3(CO)_9(CCO)]^{2-}$ (III) was stirred with a slight molar excess of $Fe_2(CO)_9$ in THF and the rapid formation of the known anionic four-metal carbide, II, was observed. In a similar fashion, labile group 6 carbonyl moieties add to III (eq 2) and IV. The products IVa,b, are produced in high yields and as described below are formulated with the butterfly structure having an exposed and reactive carbide ligand.



(2)

III

IVa; M = Cr
b; M = W

All of the members of IV display a low-field resonance in the ^{13}C NMR indicative of a carbide, and analytical data fit the proposed formulas.[9] A crystal of the $AsPh_4^+$ salt of IVb was investigated by X-ray diffraction, but disorder of the CO ligands precluded refinement of their positions. The results do however allow the disposition of the metal atoms in the framework to be specified with reasonable confidence (R = 12.3%). As indicated in structure IV the tungsten atom occupies a hinge position in the butterfly array. In keeping with this formulation, treatment of these compounds with strong acid leads to a disappearance of the carbide resonances, and new ^{13}C resonances appear with chemical shifts and coupling constants close to those of $HFe_4(CO)_{12}(CH)$ (eq 3).[10] In addition, mass spectroscopic data for $HFe_3W(CO)_{13}(CH)$ fit the proposed formulation.[11] Upon addition of methanol to a methylene chloride solution of compound V the methyne proton is lost as indicated by ^1H NMR and the cluster becomes a monoanion as judged by CO stretching frequencies. Thus the methyne proton in V is very acidic. These results provide the first examples of heterometallic clusters containing reactive carbide ligands.

$$[Fe_3W(CO)_{13}C]^{2-} + 2H^+ \rightarrow HFe_3W(CO)_{13}(CH) \quad (3)$$

In contrast, when III is treated with $Co_2(CO)_8$ an almost instantaneous reaction occurs at room temperature, producing a monoanionic cluster in high yield along with $[Co(CO)_4^-]$ and $Fe(CO)_5$. This compound displays no low-field ^{13}C NMR resonances characteristic of a carbide, but instead the NMR spectrum is reminiscent of the ketenylidene III.[12] The resonance at 82.8 ppm is broadened due to coupling with the cobalt quadrupole but the resonance at 172.5 ppm is sharp and the ^{13}C satellites can be clearly distinguished. The existence of a carbon–carbon bond is confirmed by selective irradiation of the resonance at 82.8 ppm and observation of the collapse of the ^{13}C satellite at 172.5 ppm. The elemental analysis is consistent with only two irons and one cobalt per cluster suggesting reaction 4.[12]

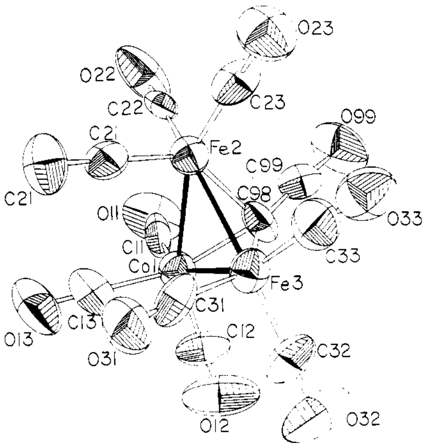
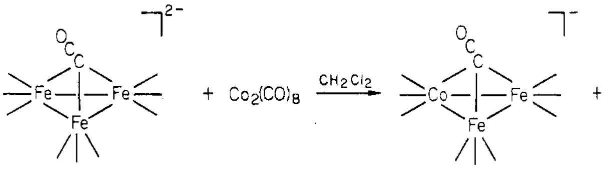


Figure 1. ORTEP diagram of the $[Fe_2Co(CO)_9(CCO)]^-$ ion in $[PPN][Fe_3Co(CO)_9(CCO)]$. The ketenylidene ligand is C98, C99, O99. It was not possible to differentiate Fe from Co so the cobalt position is arbitrary.



III

VI

$[Co(CO)_4]^- + Fe(CO)_5$ (4)

The nature of compound VI is positively established by an X-ray crystal structure determination (Figure 1) which reveals a structure similar to that of III,[13] with a CCO tilted toward the metal plane. This contrasts with the CCO which is perpendicular to the M_3 plane in $H_2Os_3(CO)_9(CCO)$[14] and proposed for $[Co_3(CO)_9(CCO)]^+$.[15] Two independent $[CoFe_2(CO)_9(CCO)]^-$ clusters are present in the asymmetric unit, and these are similar in structural detail. Both show the ketenylidene bound to the face of the metal triangle, and three terminal CO ligands are bound to each of the metals. Metal–metal distances [range 2.527 (6)–2.545 (4) Å] are consistent with those observed for $[Fe_3(CO)_9(CCO)]^{2-}$ where the average Fe–Fe distance is 2.569 (4) Å.[13] The CCO ligand in VI is bound asymmet-

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(9) For $PPN_2[Fe_3CrC(CO)_{13}]$: Anal. Calcd for $C_{86}H_{60}N_2O_{13}P_4Fe_3Cr$: C, 61.75; H, 3.62; N, 1.67; Fe, 10.02; Cr, 3.11. Found: C, 59.19; H, 3.50; N, 1.61; Fe, 8.88; Cr, 3.34. IR ν_{CO} (CH_2Cl_2) 1961 (s), 1940 (s), 1900 (m, sh), 1878 (sh), 1831 (w), 1780 (w, br) cm^{-1}. ^{13}C NMR (CD_2Cl_2, −90 °C) 483.4 (s), 233–214 (m) ppm. For $PPN_2[Fe_3WC(CO)_{13}]$: Anal. Calcd for $C_{86}H_{60}N_2O_{13}P_4Fe_3W$: C, 57.24; H, 3.35; N, 1.55; Fe, 9.28; W, 10.19. Found: C, 55.42; H, 3.00; N, 1.49; Fe, 9.13; W, 11.93. IR ν_{CO} (CH_2Cl_2) 2010 (m, sh), 1976 (vs), 1962 (vs), 1948 (s, sh) cm^{-1}. ^{13}C NMR (CD_2Cl_2 −90 °C) 470.3 (J_{C-W} = ca. 62 Hz), 221–212 (m) ppm.

(10) For $HFe_3W(CO)_{13}CH$: IR ν_{CO} (hexane) 2056 (s), 2044 (vs), 2035 (s), 2022 (m), 2010 (m), 1983 (s), 1963 (w), 1920 (w, br) cm^{-1}. ^1H NMR (toluene-d_8 25 °C) −0.51, −16.1 ppm. ^{13}C NMR (CD_2Cl_2, −90 °C) 339.7 (J_{C-H} = 97 Hz), 212–206 (m) ppm.

(11) Parent ion isotopic envelope at m/e 730 yields a good isotopic fit to the formula $HFe_3W(CO)_{13}(CH)$ (R = 9.5% assuming 23% hydrogen loss) as determined by the computer program MASPAN.

(12) For $PPN[CoFe_2(CO)_9(CCO)]$: Anal. Calcd for $C_{47}H_{30}NO_{10}P_2Fe_2Co$: C, 56.38; H, 3.02; N, 1.40; Fe, 11.15; Co, 5.89. Found: C, 56.26; H, 3.03; N, 1.27; Fe, 8.89; Co, 4.73. IR ν_{CO} (CH_2Cl_2) 2001 (s), 1990 (s, sh), 1966 (m, sh), 1930 (w), 1835 (w, br) cm^{-1}. ^{13}C NMR (CD_2Cl_2, −90 °C) 213.5 (br), 172.5 (doublet on singlet), 82.8 (br) (J_{C-C} = 79.4 Hz) ppm.

(13) Crystal data for $[PPN][CoFe_2(CO)_9(CCO)]$: Unit cell dimensions, a = 18.360 (7) Å, b = 16.370 (7) Å, c = 20.567 (12) Å, α = 76.16(4)°, β = 103.40(4)°, γ = 65.85 (3)°, V = 4529.9(3.7) Å, space group $P1$ (Z = 4, density (calcd) = 1.47 g/cm^{-1}). Mo radiation, λ = 0.71069 Å; 4327 observed reflections were collected by using θ–2θ scan mode. The structure was solved by direct methods. The refinement did not permit differentiation between Fe and Co. The metal–metal distance show only statistical differences (range 2.526 (6)–2.546 (5) Å) and metal carbonyl carbon differences are approximately equal. The final cycle of refinement led to the final agreement factor R = 8.6%. The structure of III has been redetermined with good accuracy (Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.*, in press).

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rically to the triangular face, with a 24° tilt of the least-squares line through the CCO relative to the perpendicular to the metal triangle. The CCO is more nearly perpendicular in the CoFe$_2$ compound than in the Fe$_3$ analogue, III, where a 33.5° tilt is observed. In both structures the CCO ligand tilts toward the metal atom to which the α-carbon of CCO displays the longest distance. Metal replacement reactions similar to that in eq 4 have been observed for several different clusters containing a capping ligand.[16,17] In comparison to these other examples of metal substitution, the reaction observed here is unusually facile.

Compound VI displays a reactivity pattern which is similar to that of the one other anionic ketenylidene, III. Thus protonation generates a methylidyne with simultaneous migration of the ketenylidene CO into a bridging position on the metal framework.[18] The mononegative iron–cobalt cluster, VI, is significantly less reactive than the dinegative Fe$_3$ cluster, III. For example, it shows no reaction with CH$_3$I nor is there any apparent reaction with excess Co$_2$(CO)$_8$ overnight at room temperature.

In summary, the present work provides the first examples of mixed-metal exposed carbide clusters and the first example of a mixed-metal ketenylidene. These were prepared by cluster building and metal substitution reactions on [Fe$_3$(CO)$_9$(CCO)]$^{2-}$. Similar reactions between III and labile transition-metal organometallics are likely to yield a broad class of clusters which have reactive carbon ligands.

Acknowledgment. This research was supported by NSF Grant CHE-8204401. The ^{13}C–^{13}C NMR decoupling experiment was performed at the University of Illinois NSF Regional Instrumentation Facility. The mass spectroscopy analysis program MASPAN was kindly provided by M. Andrews and H. D. Kaesz, UCLA.

Registry No. II, 74792-04-4; III, 87698-62-2; IVa·2PPN, 88669-42-5; IVb·2PPN, 88657-60-7; IVb·2AsPh$_4$, 88657-61-8; V, 88657-62-9; VI·PPN, 88657-64-1; Fe$_2$(CO)$_9$, 15321-51-4; Cr(CO)$_3$(NCCH$_3$)$_3$, 16800-46-7; W(CO)$_3$(NCCH$_3$)$_3$, 16800-47-8; [HFe$_3$W(CO)$_{13}$C]$^-$, 88657-65-2; Co$_2$(CO)$_8$, 10210-68-1; CoFe$_2$(CO)$_{10}$(CH), 88657-66-3.

Supplementary Material Available: Complete listings of positional parameters, anisotropic thermal parameters, bond angles, bond distances, and observed and calculated structure factors for [PPN][Fe$_2$Co(CO)$_9$(CCO)] and [AsPh$_4$]$_2$[Fe$_3$WC(CO)$_{13}$] (115 pages). Ordering information is given on any current masthead page.

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(18) For [CoFe$_2$(CO)$_{10}$CH]: IR ν_{CO}(hexane) 2051 (vs), 2035 (s), 2013 (m), 1864 (m), 1853 (m) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$ −90 °C) 12.72 ppm; ^{13}C NMR 269.8 (1), 250.3 (1), 207.3 (6), 200.0 (3) (J_{C-H} = 170.5 Hz) ppm.

Oxidation of Alkenes by d^0 Transition-Metal Oxo Species: A Mechanism for the Oxidation of Ethylene by a Dioxochromium(VI) Complex in the Gas Phase

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Summary: Reaction of ClCrO$_2^+$ with ethylene in a selected ion flow tube gives product ions deriving both from oxygen transfer and from cleavage of the alkene. The results are interpreted in terms of the Sharpless–Goddard–Rappè mechanism of oxidation of alkenes by Cl$_2$CrO$_2$ involving oxametallacyclobutane formation followed by reductive elimination of an epoxide (oxygen transfer) or metathesis to give formaldehyde and a Cr(VI)–oxo carbene (cleavage).

Oxidation of alkenes by d^0 transition-metal oxo species such as OsO$_4$, RuO$_4$, MnO$_4^-$, and Cr(VI) oxo complexes is of central importance in preparative organic chemistry. Since the relatively recent proposal by Sharpless[2] that metal–carbon bonded intermediates may be involved in these reactions, considerable interest in the mechanism of oxidation of alkenes by these high-valence oxo complexes has also been generated. Chromium oxo oxidation of alkenes gains a special significance in this regard, since the study of reactions of this type has a particularly long history, and the chemistry evidenced is very rich indeed.[2-4]

An understanding of the mechanism of oxidation of alkenes by Cr(VI) oxo species is hindered by the fact that diverse solvents and ligands have been utilized in the various experimental studies reported, and these factors can have a dramatic effect on the course of the reaction. In order to gain a better insight into the intrinsic reactivity of chromium dioxo species with alkenes we undertook a study of the reactions of some chromium oxo cations with ethylene and oxirane in the gas phase.[5] This work represents to our knowledge the first gas phase study of the reactions of any high-valence metal oxo species with alkenes.

Electron impact on chromyl chloride (95 eV) in the low-pressure source of a selected ion flow tube (SIFT) gives large quantities of Cr$^+$, CrO$_2^+$, ClCrO$^+$, and ClCrO$_2^+$. The SIFT technique allows clean injection of any one of these ions into the flow tube for the study of its reactions with neutral reagents. In particular, ClCrO$_2^+$ reacts very rapidly with ethylene to give two product ions resulting from oxygen transfer (C$_2$H$_3$O$^+$, 75%, and ClCrO$^+$, 12%) and one product containing both chromium and carbon (ClCrOCH$_2^+$, 13%).[6]

The mechanistic questions surrounding the reaction of Cr(VI) oxo species with alkenes seem to focus on the topology of the important intermediates or transition states. Specifically, experimental work by Sharpless[2] and very recently by Kochi[4] indicates that a primary process in the oxidation of alkenes by X$_2$CrO$_2$ (X = Cl or ONO$_2$) in solution is formation of the epoxide with retention of configuration. While even the oxidation state of the metal in the oxidant is controversial,[4] an exceedingly interesting mechanistic question, which extends to many oxidation processes, is well illustrated by the mechanistic proposals shown in Schemes I and II for the oxidation of ethylene by ClCrO$_2^+$ (1).

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(6) A single measurement of the rate constant for this reaction gave $k = 1 \times 10^{-9}$ cm^3 particle^{-1} s^{-1}. Stevens and Beauchamp (Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449–6450) have observed products analogous to ClCrO$^+$ and ClCrOCH$_2^+$ in the reaction of MnO$^+$, a d^4 species, with ethylene.

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